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Section 1 Studies Related to Biochemical Fuel Cells

Principal Investigator - Dr. J. O'M Bockris

A. Lactic Dehydrogenase in BFC

Introduction

The mechanisms of the biochemical fuel cells (BFC) can be divided into two major categories: indirect and direct BFC's. In the direct type of BFC the function of the microorganisms or enzymes is to convert without extensive loss of energy, and energy rich, but slowly reacting fuel to a highly reactive one. In this type of BFC the biochemical process and the electrode reaction could be separated in space and time, though of course, this would be not always practical. In the direct BFC the enzyme—substrate complex being in an activated and thermodynamically less stable state would react with the electrode. An intermediate approach would be to have coenzymes react with the electrode in a cyclic process, where a coupled enzyme reaction would regenerate the coenzyme to its active state. Until now BFC's of the indirect type have been constructed and investigated, but the two other mentioned types could not be demonstrated convincingly, though they are theoretically possible.

Our last status report described experiments conducted on half-cells utilizing the formic hydrogenlyase reaction of Escherichia coli. It has been established that this half-cell reaction belongs to the indirect type of BFC's. Because of the great theoretical and practical importance of this problem, in the past month we concentrated our efforts to select and investigate systems which were hoped to work as BFC's of the direct type. As indicated in our previous status report, we selected reactions involved in the glucose breakdown pathway, since glucose, especially in its polymerized form (starch, cellulose) is a readily available fuel.

Experiments on the lactic dehydrogenase system applied as direct BFC

Lactic acid is one of the final breakdown products of glucose. It can be reversibly oxidized to pyruvate in the following reaction:

$$\text{Lactate} + \text{DPN} \rightleftarrows \text{Pyruvate} + \text{DPNH}_2$$

The reaction is catalyzed by the enzyme lactic dehydrogenase. One form of this enzyme prepared from rabbit muscle is readily available commercially in a relatively pure form. Since high enzyme concentrations were necessary this was a definite advantage.

The cell (Fig. 1) consisted of three compartments. The working electrode compartment was designed as small as possible (35 ml) to save enzyme material and was surrounded by a water jacket, which was connected to a water circulating Haake thermostat. A cylindrical platinized platinum gauze electrode having a geometrical surface of 19.6 cm^2 was fitted into this compartment. Inside the cylindrical electrode a small magnetic stirring bar was placed and driven with a magnetic stirrer placed underneath the cell. The counter electrode compartment was separated by a glass sinter plate. The reference electrode compartment was separated by a stopcock. A Luggins capillary extended from this compartment to the surface of the working electrode. Through proper connections the cell could be flushed with prepurified nitrogen to creat anaerobic conditions. Temperature was maintained at 37 C. The cell was driven with an external power source. (Electro Products Lab. Model EC-2) The current was regulated by a Clarostat 240 C power resistor. A Simpson microammeter, a Kethly 610 A electrometer and an Esterline Angus recorder was used for the recording of voltage and current.

Ten mg lactic dehydrogenase enzyme (Sigma, rabbit muscle, Type II) was used in each experiment. This amount of enzyme was able to convert in the presence of sufficient DPN 4000 μM pyruvate to lactate per minute as measured spectrophotometrically. It was understood that the reaction on the electrode surface (a two phase system) will be probably several orders of magnitude slower.

Under physiological conditions the equilibrium of the reaction is far on the side of lactate production. Therefore, if one wants to direct the reaction towards pyruvate production, one has to raise the pH and has to remove pyruvate from the equilibrium. This can be achieved with a special buffer consisting of glycine and hydrazin hydrate (pH = 9.0). Lactic acid was added as sodium salt (0.2) molar solution). Coenzyme (DPN) was not added to the system, the anodically charged platinized platinum electrode was expected to function as an electron sink for the enzyme substrate complex thus establishing a direct biochemical fuel cell. Measurements were made in steady state at increasing current densities. Overpotential was plotted against log. of current density.

No satisfactory results could be obtained with the described system because of the high reactivity of the hydrazine hydrate. The platinized platinum apparently catalyzed the breakdown of this compound, and this reaction made the registration of the slower lactate conversion impossible. No suitable alternative could be found to remove pyruvate from the equilibrium without complicating the system extensively, and in order to be able to interpret the readings properly the system had to be kept as simple as possible. Therefore, it was decided to run the reaction in the opposite direction, that is, to convert pyruvate into lactate at the cathodically charged working electrode. This system, though unpractical with respect to energy-production, seemed to be more suitable for the observation of the direct enzyme-electrode reaction. Under conditions close to physiological (0.1 M phosphate buffer pH = 7.4) pyruvate is converted almost quantitatively into lactate by lactic dehydrogenase. The necessary electrons were expected to be supplied by the cathodically charge electrode. As substrate a 0.2 M sodium pyruvate was used, otherwise the experimental conditions were similar to the previous ones.

In control experiments pyruvate in absence of the lactic dehydrogenase reacted slowly with the platinized platinum cathode. It was expected, that addition of the enzyme would increase the rate of the reaction, however, this could not be observed. The addition of the enzyme did not change the reaction rate significantly, indicating that the enzyme-substrate complex does not react with the electrode or at least does not react more readily than the pyruvate alone (Fig. 2).

Several factors might be responsible for this behavior: the large size of the enzyme molecule (most fuel molecules have a molecular weight within the order of magnitude of $10^1 - 10^2$g, protein molecules however have molecular weights of $10^5 - 10^6$g), orientation problems of the active site, permanent attachment of the enzyme molecules to the electrode, etc. The material of the electrode itself may be also a decisive factor.

The nonenzymatic reduction of pyruvate probably affects the carboxyl group, reducing it to aldehyd or alcohol. It could be demonstrated that reduction does not affect the α-keto group. Lactate formation could not be demonstrated analytically.

B. Electrochemical Properties of DPN, DPNA

In general, the reactions involved in biological oxidation of carbohydrates have been well studied and a scheme for most of the reactions sequences involved has been thoroughly mapped. There are two general categories of enzymes involved in the oxidation of carbohydrates. One category contains the dehydrogenase enzymes. The other category contains the flavoproteins and the cytochromes. Usually the dehydrogenase enzymes catalyze the transfer of hydrogen plus electrons from one relatively simple organic substrate to another. The ease of solubility of the dehydrogenases in water and their relatively high degree of stability has allowed the dehydrogenase enzymes to be the best studied enzymes of the respiratory chain. The typical dehydrogenase enzymes require a cofactor for activity. This cofactor is either diphosphopyridine nucleotide (DPN) or triphosphopyridine nucleotide (TPN). An important characteristic of active dehydrogenase enzymes is the presence of sulfhydryl groups, some of which are essential to enzymatic activity. The groups are easily oxidized and must be protected under in vitro conditions by such agents as cysteine and 2-3, dimercaptopropanol. Although of little importance to fuel cell work, one very important property of some dehydrogenases is the ability to phosphorylate the oxidation product which results from their catalytic activity. An example of such a reaction is found in the catalytic phosphorytation of the oxidized form of D-glyceraldehyde-3-phosphate to D-1, 3-diphosphoglveeric acid by glyceraldehyde-3-phosphate dehydrogenase. Such a reaction is highly important to the energy economics of living systems.

Because the pyridine nucleotides DPN and TPN are essential to the activity of the dehydrogenase enzymes, some of their properties must be discussed. Both DPN and TPN are characterized by an absorption band with a maximum of 260 mμ. This band is due to the presence of adenosine. Upon reduction of DPN and TPN an absorption band appears at 340 mμ. This absorption band is due to the presence of the reduced nicotinamide derived quaternary pyridinium moiety of DPN and TPN.

The significant difference in the absorption spectra of reduced and oxidized DPN and TPN allows one to determine the oxidation reduction state of this compound by spectrophotometric methods. Although DPNH and TPNH can be oxidized by ferricyanide and other organic compounds, the pyridine nucleotides are not oxidized by molecular oxygen.

The dehydrogenase enzymes actually catalyze bimolecular reactions. For example, when alcohol dehydrogenase catalyzes the oxidation of ethanol to acetaldehyde the enzyme simultaneously catalyzes the reduction of DPN. It is of interest to note that under anaerobic conditions alcohol dehydrogenase and acetaldehyde are responsible for regenerating DPN and DPNH. Thus, in anaerobic respiration, simple organic compounds act as hydrogen and electron sinks. The final by-products of fermentation are organic acids, whereas in aerobic respiration, carbon dioxide and water are produced. Dehydrogenases are the terminal electron transferring enzymes in fermentation.

Although, as in the case of some microorganisms, reduced flavoproteins can be oxidized at the expense of some organic compounds, these enzymes are usually reduced by DPNH or TPNH and are oxidized by the cytochrome enzymes. When oxygen acts as the final electron acceptor in respiration the flavoproteins accept hydrogen and electrons from DPNH and TPNH and transfer electrons to the cytochromes. Thus the flavoproteins not only act as an intermediary between the dehydrogenases and the cytochromes but also function as agents which share properties of both the dehydrogenases and the cytochromes. That is, the flavoproteins can accept hydrogen plus electrons from the dehydrogenases and transfer only electrons to the cytochromes. The hydrogen nucleous is usually transferred from the flavoproteins to the cellular environment as a proton. The functional groups of the flavoproteins are organic heterocyclics such as flavin mononucleotide (FMN) and flavin adenine dinucleotide (FAD). The function of the flavins as electron transporters is attributable to the reversible reduction of the isoalloxazin ring. The reaction

mechanism for reduction of the flavins is similar to that of the reduction of tetraphenyl-p-quinonediimine. In respect to electrochemistry, it is of interest to note that the E'_0 (pH 7, 30°C) of unbound FMN is -0.219 volt as compared to the E'_0 (pH 7, 30°C) of -0.123 volt when FMN is bound to glucose -6- phosphate oxidase. This shift in potential increases the rate at which FMN oxidizes TPNH. The E'_0 of the TPN system is -0.320 volt as pH 7 and 30°C. The flavins are electrochemically active to such an extent that the E'_0 of reduced and oxidized flavins can be measured directly. Two important reasons that the flavoproteins are not suitable for electrochemical studies are: (1) The enzymes are difficult to isolate and purify, and (2) a multienzyme system would be required for electrode kinetic studies.

The cytochrome enzymes are characterized by the function of accepting electrons from the flavoproteins and transferring these electrons to molecular oxygen. While the electron transferring functional groups of the dehydrogenases and flavoproteins can be readily removed from their protein moieties ("apoenzyme") the iron-porphyrin prosthetic groups of the cytochromes are more intimately bound to the apoenzymes. For example, the porphyrin group of cytochrome c is joined to the protein by two thioether linkages. The cytochromes a and b do not react directly with molecular oxygen under <u>in vivo</u> conditions. The inability of cytochrome c to react with molecular oxygen or carbon monoxide is attributed to the fact that the six coordinate valences of cytochrome c iron are satisfied by four porphyrin nitrogens, and by two of the imidazolyl groups of the protein. Cytochrome oxidase is the enzyme responsible for accepting electrons from reduced cytochromes c and a. The porphyrin prosthetic group of cytochrome oxidase has a structure similar to that of hemoglobin and is thus able to combine directly with molecular oxygen.

Although the structure of the cytochromes and other oxidases is most amenable to electrochemical studies, disadvantages are found in the facts that only cytochrome c is both stable and easily isolated. Also, the cytochrome systems can, at best, be studied electrochemically in the form of multienzymes systems.

Thus it is clear from the above discussion that although the dehydrogenases are not the most electrochemically active of the respiratory enzymes, those properties such as ease of isolation and purification (availability), low oxidation reduction potentials, and stability make, at least, a preliminary electrochemical study worthwhile. The preliminary study described in this report involves galvanostatic reduction of DPN, galvanostatic oxidation of DPNH, coulombic yield determinations of the oxidation of DPNH and reduction of DPN, and a comparison of the electrochemical properties of DPN and DPNH in the presence and absence of a suitable enzyme.

Methods and Materials

A three compartment cell having a working volume of 100 ml was designed and fabricated. The cell was designed so that temperature could be regulated by means of an internal heating coil. Water was circulated through the coil by means of a Haake circulating water bath. The top of the cell was fabricated in such a manner that ports were provided for intrusion of a thermometer, and for emplacement of a syringe for, if necessary, addition of substrates or enzymes. Current was supplied by means of a D.C. power supply. A standard saturated calomel electrode was used as the reference electrode for measuring the potential of the working electrode. The counter electrode compartment of the cell was separated from the working electrode compartment by a coarse sintered glass fritt. An outlet with a stopcock was provided at the bottom of the cell for sample removal. Gas inlets were provided and so positioned that gas could be bubbled through the solution, or passed over the solution when protein was present. A Simpson Model 269 milliameter was used for measuring current. Voltage was measured with Keithley Model 610A electrometer and was recorded on an Esterline Angus Graphic Ameter Model A. W. Stirring was accomplished by means of a magnetic stirrer. An anaerobic environment was maintained during the course of the experiments by passing prepurified nitrogen through the cell.

The zero current rest potential of the DPN-DPNH system was determined at 37°C by adding sufficient amounts of DPN and DPNH to nitrogen saturated, 0.1 M, pH 6.1 phosphate buffer so that equal concentrations of DPN and DPNH were obtained. After addition of DPN and DPNH, the system was allowed to come to equilibrium and the open circuit potential was observed and recorded.

All current potential relationship determinations were performed with a DPN and/or DPNH concentration of 2.86×10^{-3} moles/1. The concentration of the buffer was 0.1 **M** and the temperature was 37°C in all cases. Anaerobic conditions were established and maintained throughout the experiments by bubbling prepurified nitrogen through the solutions.

In those cases involving the presence of enzymes in solution, bubbling was ceased immediately after introduction of enzyme and nitrogen was flowed through the atmosphere above the solution. The reaction system was vigorously stirred in all experiments. The independent variable, in this case current, was regulated by means of a variable resistor.

For coulombic yield studies current was maintained at a predetermined level. When determining the coulombic yield for reduction of DPN, the concentration of the reaction product (DPNH) was determined directly by spectrophotometric means at a wave length of 340 $m\mu$. The spectrophotometer employed in these studies was a Beckman Model DB. For coulombic yield determination for the oxidation of DPNH, for each one ml sample, the residual amount of DPNH was hydrolyzed by adding sufficient 1N HCl to bring the reaction sample to a pH value of approximately 1 unit. Acid hydrolysis was allowed to proceed for 10 minutes. The hydrolysate was titrated back to the original pH (6.1), 2M KCN was added, and the resulting mixtures were brought up to a constant volume of 10 ml. The optical density of the resulting DPN-CN complex was determined at a wave length of 327 $m\mu$. The particular method of analysis employed for the above determination was based on the instability of DPNH in acid solution. At a pH of 1.0, the reduced nicotinamide ring of DPNH is

destroyed with a concurrent elimination of the 360 mμ absorption peak of this compound. Since DPN is stable in acid environments, it is possible to detect the presence of DPN in the hydrolysate by forming a DPN-CN complex which absorbs at 327 mμ. It is important that the pH of the hydrolysate is adjusted to basic or near neutral hydrogen ion concentration before KCN is added, for the DPN-CN complex has the same acid instability as does DPNH.

Since differing rest potentials were noted when DPN and DPNH were studied alone the oxidation of DPNH in the presence of an equimolar amount of DPN and the reduction of DPN in the presence of equimolar (2.85×10^{-3}M) DPNH were studied. Conditions were as stated above.

Since it was noted that the open circuit potentials of DPN and DPNH differed, oxidation of DPNH with rabbit muscle lactic acid dehydrogenase (LDH) present was studied with an equimolar (2.86×10^{-3}M) amount of DPN, as was the case in respect to the concentration of DPNH when the reduction of DPN was studied in the presence of LDH. In both cases conditions were as stated above and the LDH (Sigma Chemical Co.) concentration was 100 mg/100 ml. Since the dehydrogenases, as stated above, catalyze reversibly, bimolecular reactions between a simple organic compound and DPN, the author feels that it was justifiable to study the effect of a dehydrogenase on the overpotential of the reaction of DPNH oxidation and DPN reduction when an electrode was acting as the electron sink and electron source. It should be noted here that the pH of the phosphate buffer used in the LDH studies was 7.4. This is the optimum pH for the activity of the enzyme system. As a control, a study of the anodic oxidation of LDH was performed at a concentration of 2 mg LDH/100 ml.

Results

The rest potential in a system consisting of DPN and DPNH alone at a pH of 6.1 was found to be -.130 volt versus the standard hydrogen electrode. Current - potential relationships for the oxidation of DPNH alone and for the reduction of DPN alone are shown in Fig. 1.

The results of the coulombic yield studies for the oxidation of DPNH and for the reduction of DPN revealed that, under the above described experimental conditions, neither DPNH was produced cathodically from DPN nor was DPN produced anodically from DPNH. The current-potential relationships for the oxidation of DPNH in the presence of an equimolar amount of DPN and for the reduction of DPN in the presence of an equimolar amount of DPNH are as presented in Fig. 2. The current-potential relationships for the oxidation of DPNH in the presence of an equimolar amount of DPN and 2 mg/200 ml LDH and for the reduction of DPN in the presence of an equimolar amount of DPNH and 2 mg/200 ml LDH are presented in Fig. 3.

Fig. 4 presents the data for the oxidation of 2 mg/100 ml LDH in pH 7.4 0.1 M phosphate buffer.

Discussion

The results of the determination of the rest potential of the DPN-DPNH system suggest that the belief that the DPN system is not electrochemically active on metal electrodes should be re-evaluated. If one extrapolates the relationship between the potential and pH of the DPN system plus xanthine oxidase and a mediator one arrives at a potential value of -.260 volt at a pH of 6.1. This figure does not agree with our experimental results. It may very well be that as in the case of the flavin nucleotides the potential of the DPN-DPNH system is shifted, only in this case in the opposite direction, when DPN or DPNH is complexed with a suitable enzyme.

The results of Fig. 1 indicate that both DPN and DPNH are indeed electrochemically active when no oxidase enzyme or mediator is present. The results indicate, in this case, that DPN and DPNH do not act reversibly. It is obvious from the results that upon reduction, DPN is more electrochemically active than is DPNH upon oxidation.

Results of the coulombic yield studies, however, indicate that although there is evidence for electrochemical reactions occurring in the DPN and DPNH molecule, the desired reactions are not occurring. Thus, one must assume that when DPN is reduced and when DPNH is oxidized under the above-described conditions some other

part of the molecule is undergoing oxidation or reduction. This is, of course, obvious in view of the fact that no DPNH was produced by reduction of DPN and visa versa. Unfortunately, the curves for the oxidation of DPNH in the presence of an equimolar amount of DPN and for the reduction of DPN in the presence of an equimolar amount of DPNH are such that the reversible potential for the DPN/DPNH system cannot be evaluated.

The presence of LDH proved to have little effect upon the current potential relationship for the oxidation of DPNH and reduction of DPN. This is not surprising for although the hypothetical role of the dehydrogenase enzymes is to "activate" hydrogen one must bear in mind the highly stereospecific nature of enzyme catalysis. There certainly is a great difference in the stereochemistry of organic compounds and the apparent non stereospecific nature of metal electrode surfaces.

The results indicate that, as would be expected the LDH molecule was electrochemically oxidized. Without further studies it is difficult to interpret these results. However, when one considers the complexity of structure and function of enzymes the fact that LDH is not electrochemically inert is certainly not encouraging.

Conclusions

From the above-stated results one can conclude that further electrochemical studies of the dehydrogenase enzymes may not be worthwhile. However, not all of electrochemical properties of the pyridine nucleotides have been considered in this study. There is evidence that the phosphorylation of DPN may play a significant role in the oxidation reductions of this compound. It would be of great interest to study the electrochemical properties of the proposed DPN-phosphate compound. It must be concluded, also, that if DPN and DPNH are indeed electrochemically refractory there is a possibility that electrochemical studies on the regeneration of DPN from DPNH by electrochemically oxidized compounds such as alcohol may prove to be of profound importance, not to the concept of direct biochemical fuel cell reaction, but rather to indirect fuel cell reactions.

Section 2 Plasma Physics

A. Magnetohydrodynamics

Principal Investigator - Dr. H. Yeh

Currently we are debugging our alkali metal injection system. A great number of problems have been encountered with this system. The Pyrex syringe we originally used was subject to binding and has been replaced by a polypropylene syringe. Excessive pressure drop was encountered in the tube used for boiling the potassium. We feel that this resulted from using a tube length considerably greater than required to meet the heat transfer requirement. It has been shortened to a length which more realistically corresponds to the heat transfer requirement. Further difficulties are being encountered which apparently are being caused by oxidation of the potassium in the injection system. We are installing a drier in the argon line now to eliminate traces of water that we suspect are in the argon. We are also redesigning the system to minimize contact between the potassium and traces of elementary oxygen that remain in the system.

The use of pure potassium has been a nuisance from operational considerations because of the need for heating all of our line above the melting point of potassium (62.3°C). Because of this we plan now to use a Na-K alloy which will be a liquid below room temperature.

In the last report it was mentioned that the quartz test sections had not been received from our suppliers. We now have these.

Except for the modifications noted above our research is going ahead as described in the earlier reports.

B. Thermionics*

Principal Investigators - Dr. L. Zelby
Dr. G. Schrenk

a. Semiconductor Sandwich Model

In the previous report (January, 1964), a number of models used in attempts to describe the operation of a plasma diode in the passive mode have been described. In addition to a number of common features enumerated in that report, the authors of the respective papers solved several sets of equations on a computer, adjusting various parameters to obtain the best fit with the available experimental data. This point of view obscures the significance of the physical phenomena occurring during the various states of operation of the device. In order to provide, at least partially, some answers regarding the effects of electrode spacing and sheath thickness, a relatively simple model has been assumed.

The model is analogous to the one used for a semiconductor sandwiched between two metals. One of the electrodes is assumed to be emitting electrons. Ambipolar diffusion is assumed in the sheaths of finite dimensions near each electrode, and the electron and ion density is assumed to obey the Boltzmann relation between the sheaths and bulk plasma.

Work on evaluation of the electron and ion currents as a function of the potential distribution, electrode spacing, sheath thickness, gas pressure, and emitter temperature is in progress.

*This progress report supercedes all previous research plans. Out initial review of the literature has been completed. Based upon our literature review, we are initially directing our efforts in the specified areas.

b. Emitter Surface Physics

The concept of a work function is an integral part of the theory of thermionic (plasma diode) energy converters. Researchers often use the term work function without specifying whether they mean the true, Richardson, effective, or some other type of work function.[1] The classical definition of the work function is the energy difference between the Fermi level of the metal and the energy required to remove an electron from the Fermi level to ∞.[2] By definition all these will give the correct value of electron emission; but the relationships between these various types of "work function" and the classical definition of "work function" is not clear. Clarification of this relationship is essential to an understanding of the various emission and adsorption processes in a plasma diode. Thus, as a first step to a more complete understanding of emission and adsorption phenomena, the significance and interrelationship of these various "work functions" will be studied theoretically.

In this work we will initially assume the well-known and generally accepted Sommerfeld-Nordheim model for electron emission from clean metals.[3] In this theory the metal is considered to be a free electron gas in a container. This container allows electrons of certain energies and directions to escape, i.e., to be emitted from the interior of the metal. This emission is a function of the electron gas temperature, the potential difference between an electron at the Fermi level and a free electron at infinity, and the transmission coefficient of the container. A strong electric field (greater than approximately 10^4 volts per meter) can modify the potential barrier to produce increased emission (Schottky effect).[4] For clean monovalent metals Wigner and Bardeen[5] and later Bardeen[6] have shown quantum mechanically that the work function of a metal consists basically of an image potential plus a surface double layer, the image potential being a major of that part of the work function due to the bulk properties of the metal while the surface double layer includes only the surface effects.

When a clean metal is placed in a metallic vapor, both the image potential and the surface double layer change. Levine and Gyftopoulos[7] have succeeded in correlating, macroscopically, the electron emission, adsorbate temperature, and vapor pressure with a fair degree of success for cesium on tungsten. For other emitters, however, like barium-tungsten or thorium-tungsten, their agreement is not so good.[8] This work does not lead to a detailed microscopic understanding of the concept of a work function. In fact, no detailed microscopic understanding presently exists.

We are presently investigating microscopically the precise meaning of the concept of a work function for a metal with an adsorbed metallic monolayer. Our emphasis will be on the surface rather than the bulk properties of the system.

Two possible ways for studying this composite surface are under consideration. The first is to investigate the vacuum-adsorbate and adsorbate-substrate surfaces separately. The two results would then be superimposed to give the properties of the surface and its effect on the "work function" of the system. Since the adsorbates of interest to plasma diodes are alkali metals, the vacuum-adsorbate surface can be investigated quantitatively following Bardeen's procedure for sodium.[6] The absorbate-substrate surface, however, requires further investigation.

The second approach is to predict all the effects of the composite surface on the work function at once, i.e., the vacuum-adsorbate and adsorbate-substrate effects would not be separated. This can be done by extension of Smoluchowski's variational technique for calculating the surface charge density as a function of crystalographic orientation to include the effect of an adsorbed layer.[9] The most difficult part of this extension is the selection of a physically meaningful charge distribution that is also mathematically tractable. Another possibility is the extension of Bardeen's procedure for calculating the surface double layer of sodium to this composite surface.[6] This technique would include the effects of exchange and correlation energies, neglected by Smoluchowski.

Of these three approaches Smoluchowski's work appears to be the most practical for estimating the surface double layer. The superposition of the potential of the surface double layer on a slightly modified image potential will give the shape of the barrier containing the free electron gas in the metal. On the basis of these results, a new electron emission equation will be calculated. This equation and its work function will then be evaluated on the basis of available experimental data.

c. General Analytical Work

As reported in the previous progress report (Appendix D) a theoretical model of a cesium plasma diode has been formulated.[10] This model applied to a plasma diode whenever a fully randomized plasma is formed in the interelectrode space.

The successes and limitations of this model were covered in the previous report. Perhaps its greatest limitation is the fact that it is mathematically untractable. Because of this and because of the other uncertainties in experimental inputs (volume ionization rates, etc.) attempts to obtain solutions over wide ranges of the input parameters to compare with experimental results have not been very successful.

The value of a phenomenological macroscopic model in understanding plasma diode results cannot be questioned; it cannot only assist us in correlating and predicting results but can also help us separate off "fine structure" results for further study. Thus, the advantages and shortcomings of this previous model are being used to develop a new model.

This new model is currently being used to investigate the criteria for determining if the emitter sheath is ion-rich or electron-rich. The criterion in common use[11] is determined solely by conditions at the emitter surface. If I_S = electron emission current (given by Richardson equation), I_{pE} = ion current from the emitter, and m_p, m_e = mass of ion, electron, this criterion can be written as

$$I_S/I_{pE} = \sqrt{m_p/m_e}$$

For cesium, this gives $I_S/I_{pE} = 491$. The only uncertainty usually expressed in the literature is whether or not the Saha-Langmuir equation holds for I_{pE}.[11] This criterion obviously neglects any volume ionization and/or recombination effects that take place. In a broad-spaced plasma diode, however, these effects cannot be neglected; thus, we are currently investigating this problem in order to obtain the correct criterion for determing the sign of the emitter sheath.

Our initial results show that the ratio I_S/I_{pE} is not the quantity that determines the sign of the emitter sheath when volume ionization and/or recombination effects are taken into account. For a given cesium neutral current I_a, emitter temperature T_E, collector temperature T_c, and gas temperature T_g, the most important parameters are the electron emission current I_S, net volume ionization or recombination A_{DE}, and electron plasma temperature V_{Te}. In this work the electron temperature and net volume ionization and/or recombination are treated as unknown parameters.

This work will result in a family of curves of I_{So} versus A_{DE} for V_{Te} = constant. For a given curve our criteria for the emitter sheath can be written

$$I_S > I_{So} \Rightarrow \text{electron-rich sheath}$$

$$I_S < I_{So} \Rightarrow \text{ion-rich sheath}$$

It is anticipated that these curves will be very useful in correlating experimental results as the current-voltage characteristics of a plasma diode depend rather sensitively on the sign of the emitter sheath.

This determination of criteria for specifying the emitter sheath sign is a first application of our refined macroscopic phenomenological model of a broad-spaced plasma diode. We presently plan to use this model to investigate other problem areas that will lead to a better understanding of the plasma diode. Comparisons with available experimental results will always be made whenever possible. We anticipate that this model will elucidate other problem areas for further microscopic study.

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Section 3 Thermal Energy Storage

A. Thermophysical Properties

Principal Investigator - Dr. G. Belton

(a) Experiments have been conducted to establish the phase diagram of MgF_2 + MgO by differential thermal analysis. A eutectic with MgO = 0.08 at 1230° ± 2°C has been established. There appears to be a slight error in the eutectic composition. This is due to the impurity of the MgF_2 used. The main difficulty comes from the fact that MgF_2 was found to decompose in the presence of water vapor and oxygen. The apparatus was modified in such a way that an argon atmosphere can be maintained around the sample during the experiment. The argon was purified by passing it over calcium turnings kept at 650°C in another furnace. Next, an effort was made to obtain pure MgF_2. The chemical grade of MgF_2 obtained may contain about 10% water. It was therefore dried slowly under a vacuum at 400°C. The product obtained was found to give a 20°C lower melting point. The sample after the experiment was examined under the microscope and the presence of MgO was not observed. It has as yet not been possible to find the explanation for the low melting point. In the meantime another sample was prepared by first removing the water at 400°C. The sample was leached with HF and dried first at 100°C and then at 400°C. The MgF_2 prepared in this way is not very pure, but is satisfactory. By using this material, a phase diagram has been established and the results will be communicated in detail in a technical report.

The diphenyl ether dropping calorimeter is still in the fabrication stage. Work on the construction of the furnace suitable for use up to 2300°C is in progress.

(b) Partial molar properties of the system $CaCl_2$ - $MgCl_2$ are being determined. Preparation of the chlorine electrode is the major part of the experimental set up.

Materials and equipment--magnesium chloride in anhydrous form is very hygroscopic. Crystalline magnesium chloride as supplied by Mallinckrodt contains six water molecules. This was dried by heating in a vacuum up to 500° C in 5-hours. Dried $MgCl_2$ was mixed with absolute alcohol to prevent absorption of water by the salt.

The electrolysis cell and accessories are illustrated in the accompaning diagram. All parts are made of fused quartz glass silica tube, 21" long and 38 mm. in diameter. The cell is lowered into the furnace tube until about 6" of it remains above the furnace level. Argon serves to provide the neutral atmosphere. Dry chlorine introduced, as shown, into the inner tube. This gas bubbles over the graphite electrode, rises up and escapes through the outlet in the bigger tube. The graphite rod is dipped into the melt. The lower tube is closed with a fritted glass disc which prevents direct diffusion of the salt. The graphite rod was pretreated with chlorine gas in order to reduce the time period to obtain equilibrium.

The magnesium electrode was prepared by packing reagent grade magnesium turnings above the perforated disc. Tungsten wires make the electrical contact.

The temperature of the cell is raised slowly to 800° C; the salt is then in the molten stage as its m.p. is 708° C. Chlorine is bubbled through continuously. Measurements of the e.m.f. are made with a potentiometer. From the e.m.f. values, the free energy of formation of $MgCl_2$ can be calculated. This experiment is in progress at the time of the report. The investigation of the system $CaCl_2$ - $MgCl_2$ is expected to be completed within a few weeks.

B. Heat Transfer

Principal Investigator - Dr. Manfred Altman

Several designs of suitable apparatus are being analyzed in detail. As yet no satisfactory design has been arrived at. The difficulties of making accurate heat transfer measurements above 2000° C are such that the needed apparatus becomes so complex and expensive as to make it imperative that the final design not have any hidden faults.

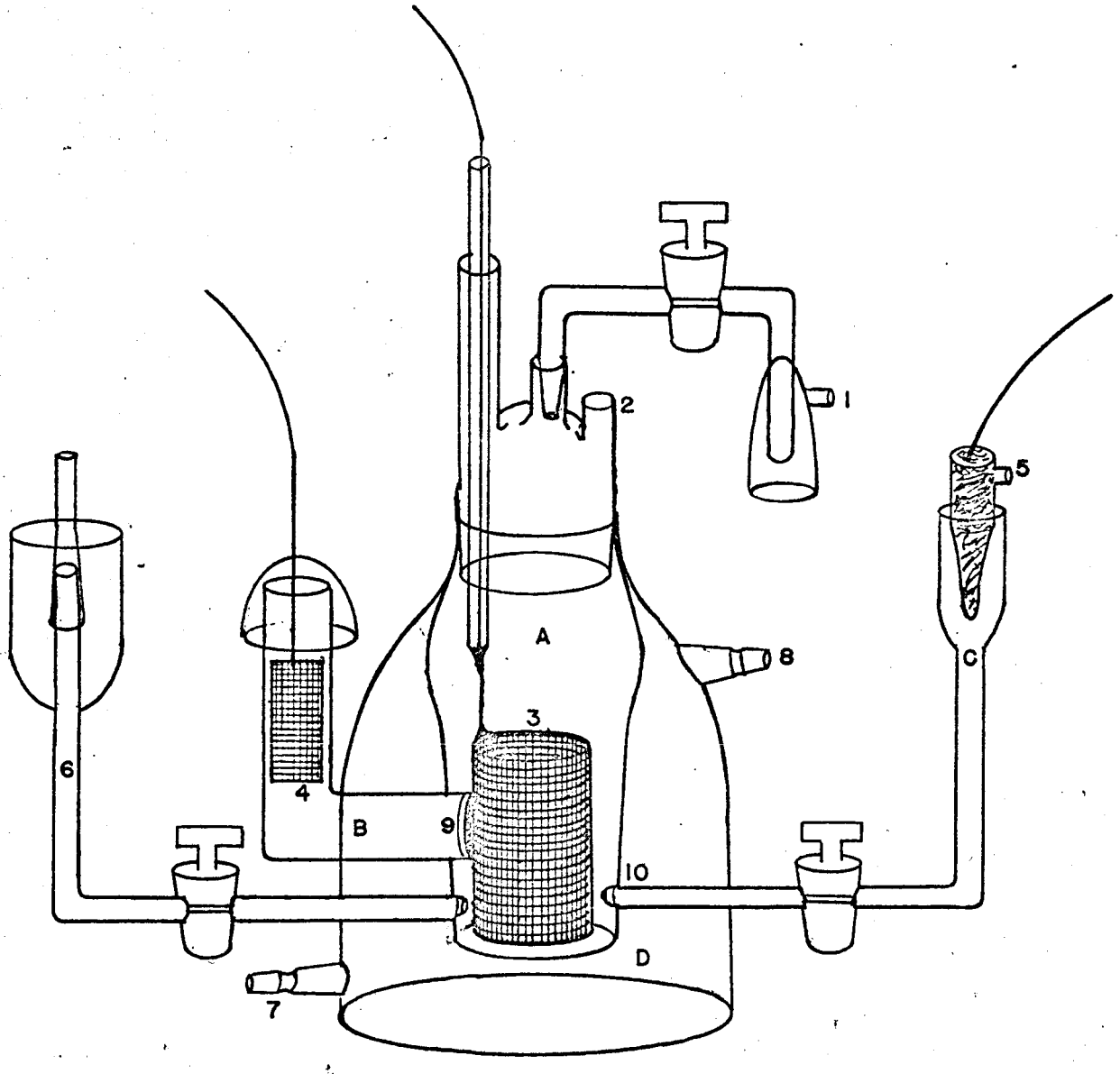
Extensive analog computer runs duplicating heat transfer in the test section are being made to study possible resolution of data, and achievable accuracy.

Considerable effort is being made in learning how to fabricate samples of different geometries, and to learn how to encapsulate them for liquid studies.

Experiments are in progress to determine the best means of double-checking temperature measurements. Two-color pyrometers and thermocouples are being investigated for this purpose.

FIG. 1

DIAGRAM OF A SMALL-VOLUME CONTROLLED TEMPERATURE CELL FOR THE STUDY OF EUZYMATIC HALF-CELL REACTIONS.



A	WORKING ELECTRODE COMPARTMENT	4	CONTER ELECTRODE
B	CONTER ELECTRODE COMPARTMENT	5	CALOMELE ELECTRODE
C	REFERENCE ELECTRODE COMPARTMENT	6	N_2 – INLET
D	WATER JACKET	7	WATER INLET
1	N_2 – OUTLET	8	WATER OUTLET
2	SYRINGE – SOCKET	9	SINTER PLATE
3	WORKING ELECTRODE	10	LUGGINS – CAPILLARY

FIG. 1.

V—LOG i RELATIONSHIP FOR OXIDATION OF DPNH ALONE AND REDUCTION OF DPN ALONE

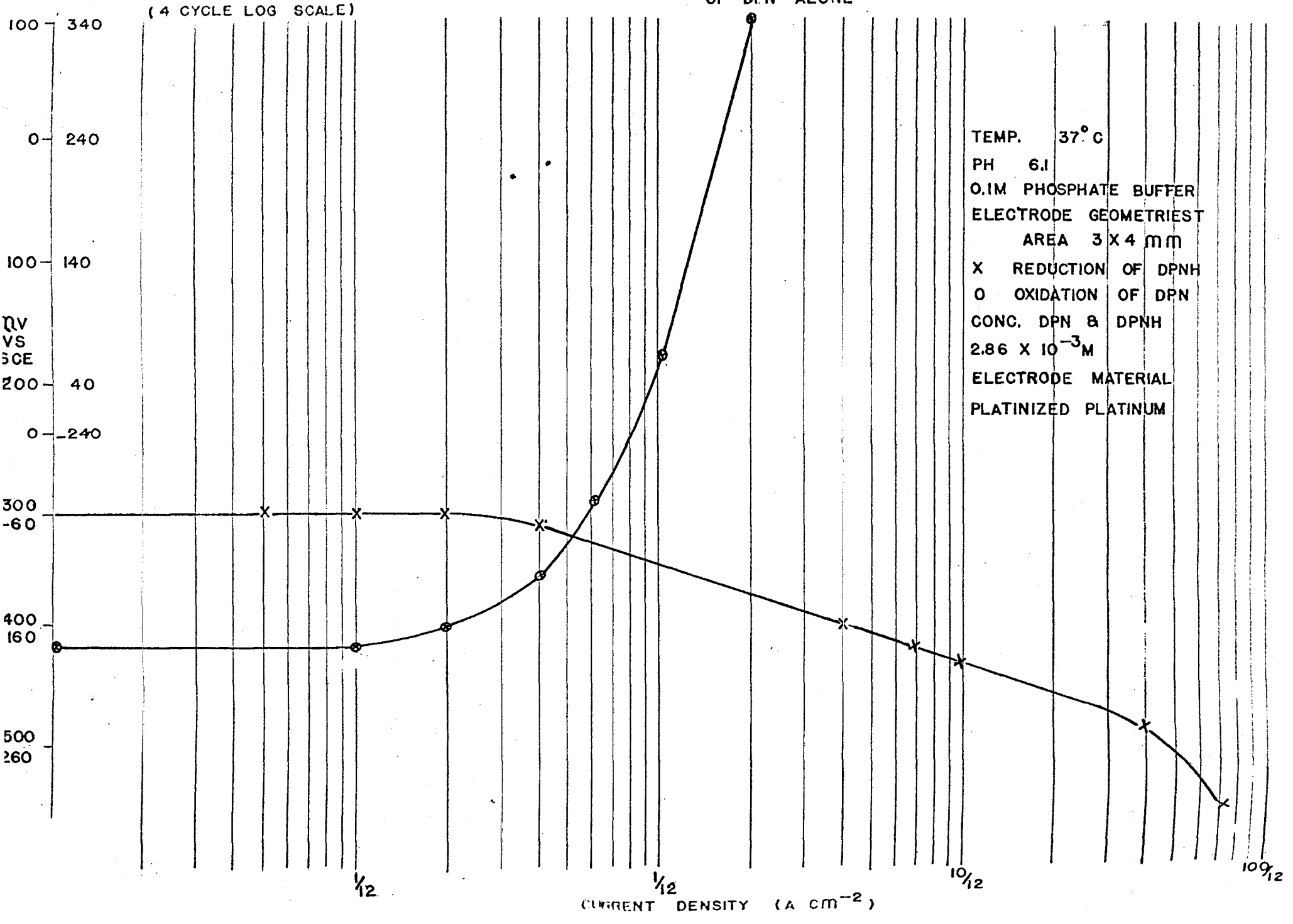


FIG. 2

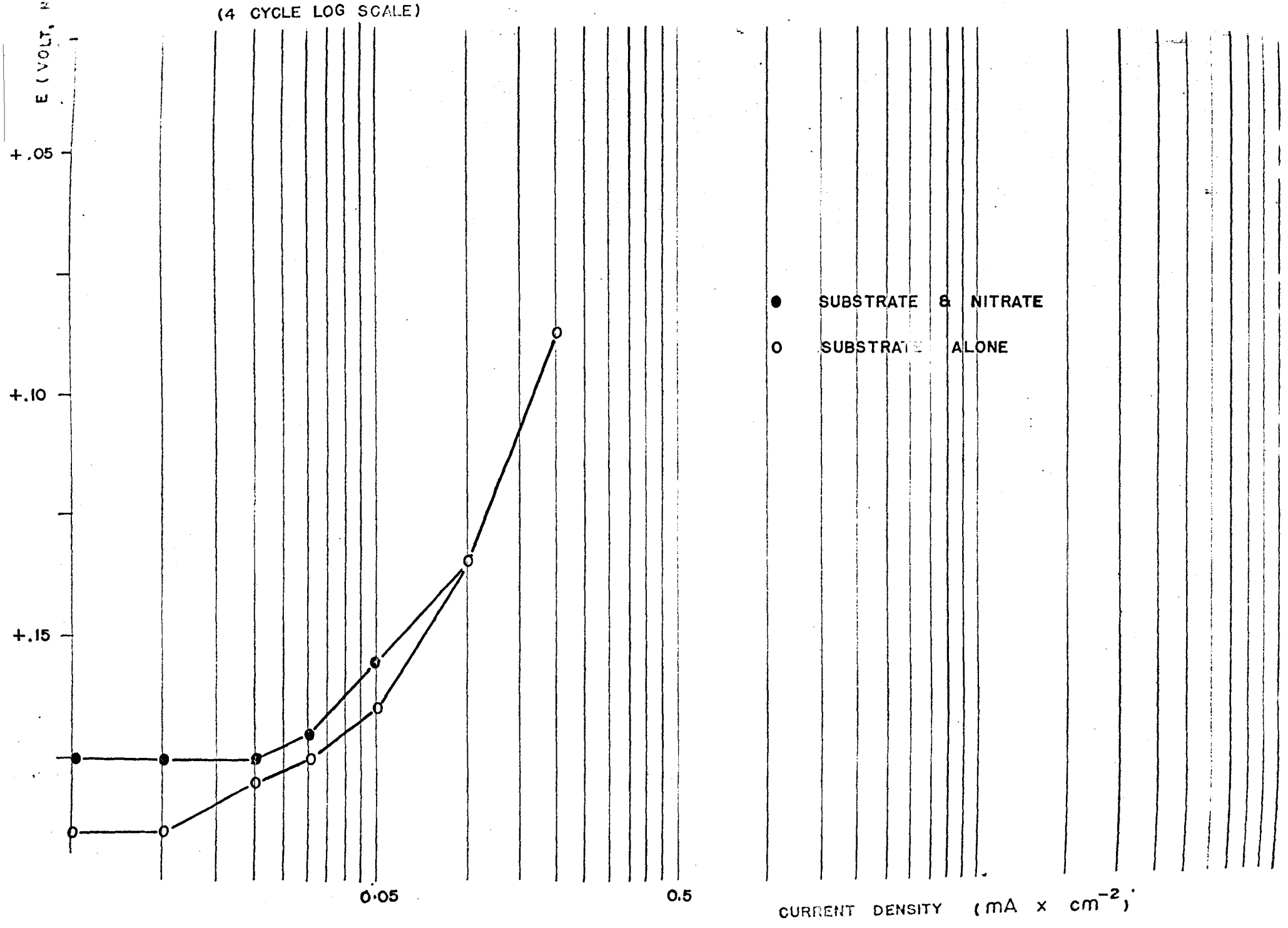

(4 CYCLE LOG SCALE)
E (VOLT, RHE)
+.05
+.10
+.15
0.05
0.5
SUBSTRATE & NITRATE
SUBSTRATE ALONE
CURRENT DENSITY (mA x cm^{-2})

FIG. 3

V—LOG i RELATIONSHIP OF OXIDATION & DPNH IN PRESENCE OF EQUIMOLAR DPN AND VISA VERSA PLUS VAD

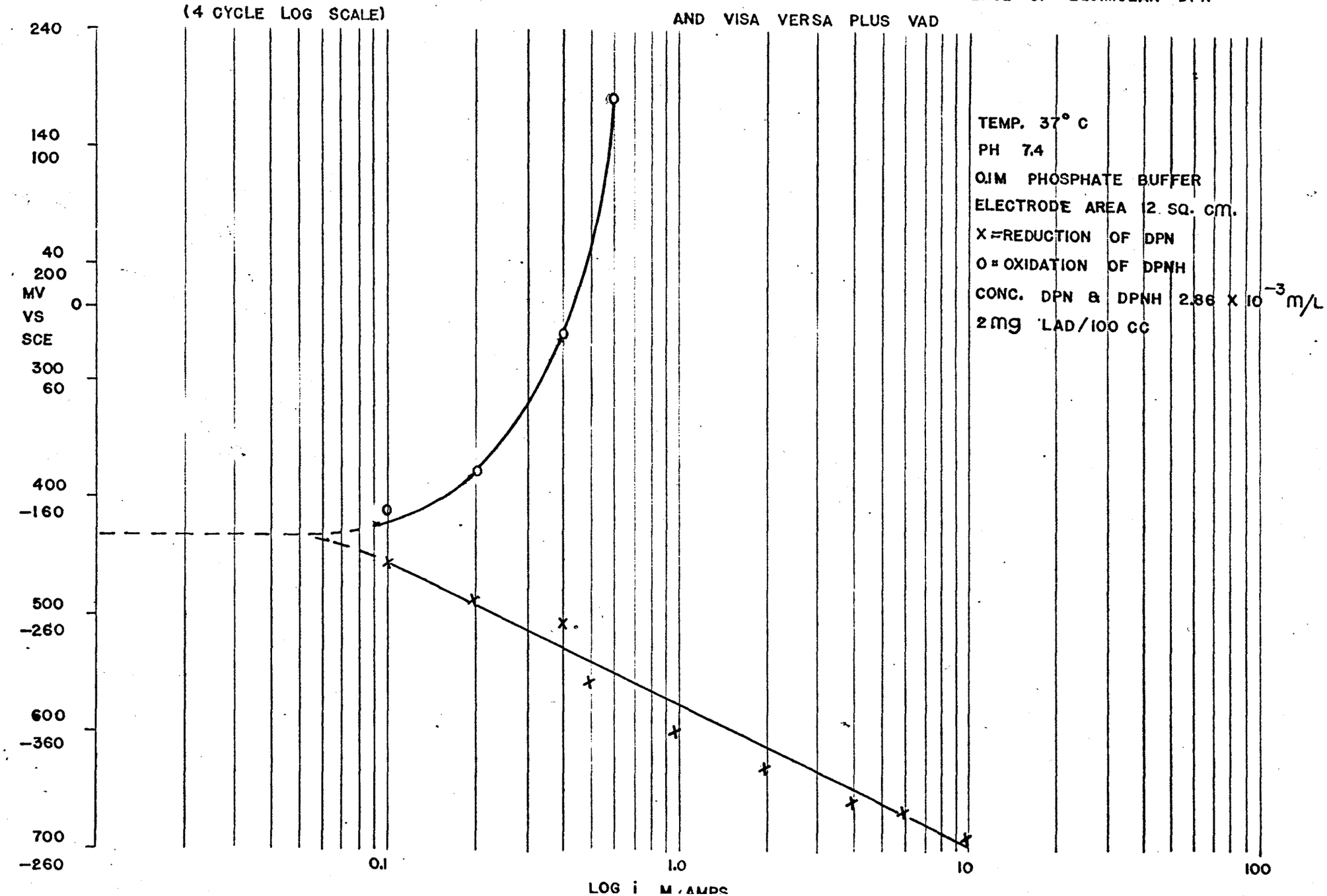
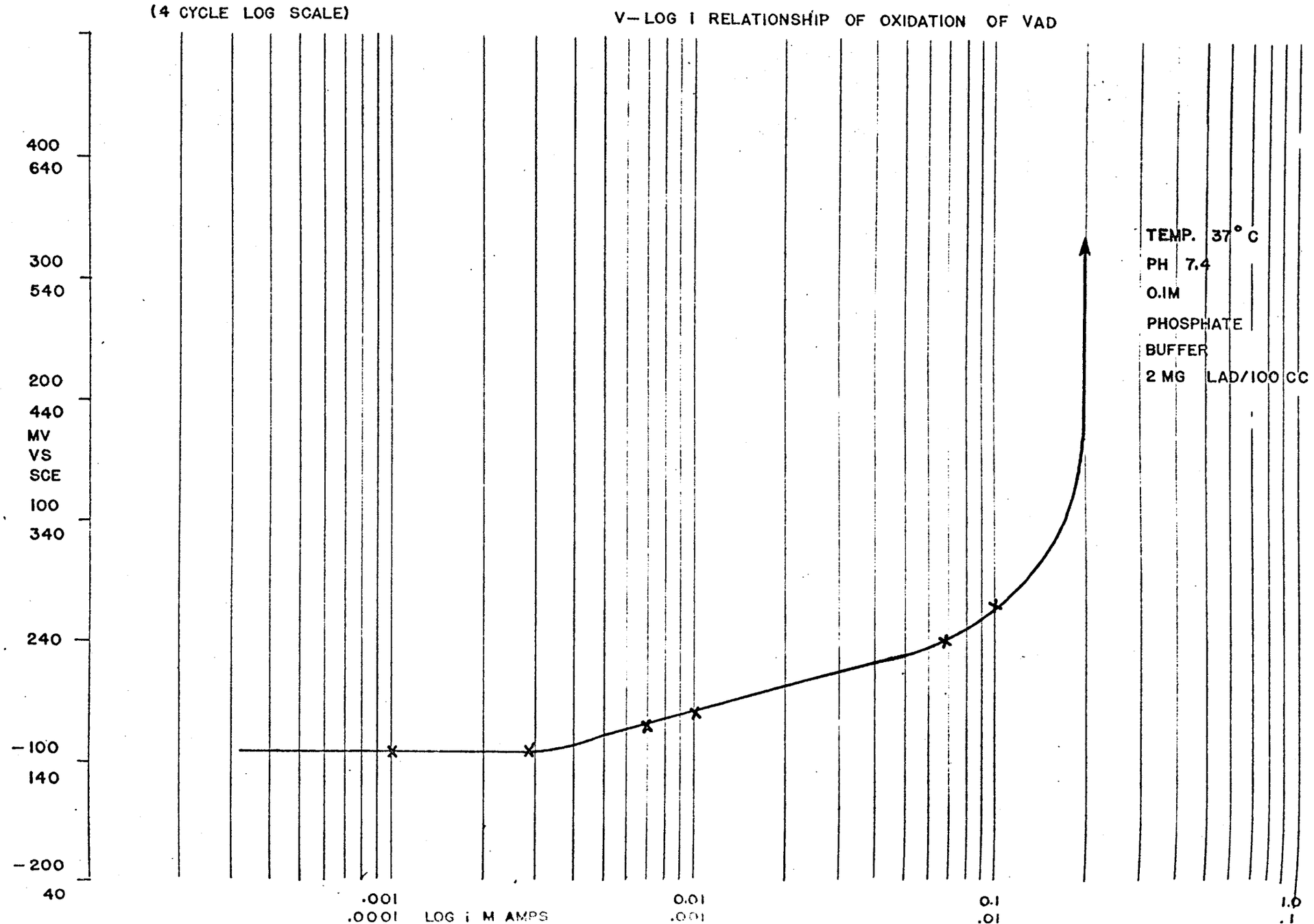
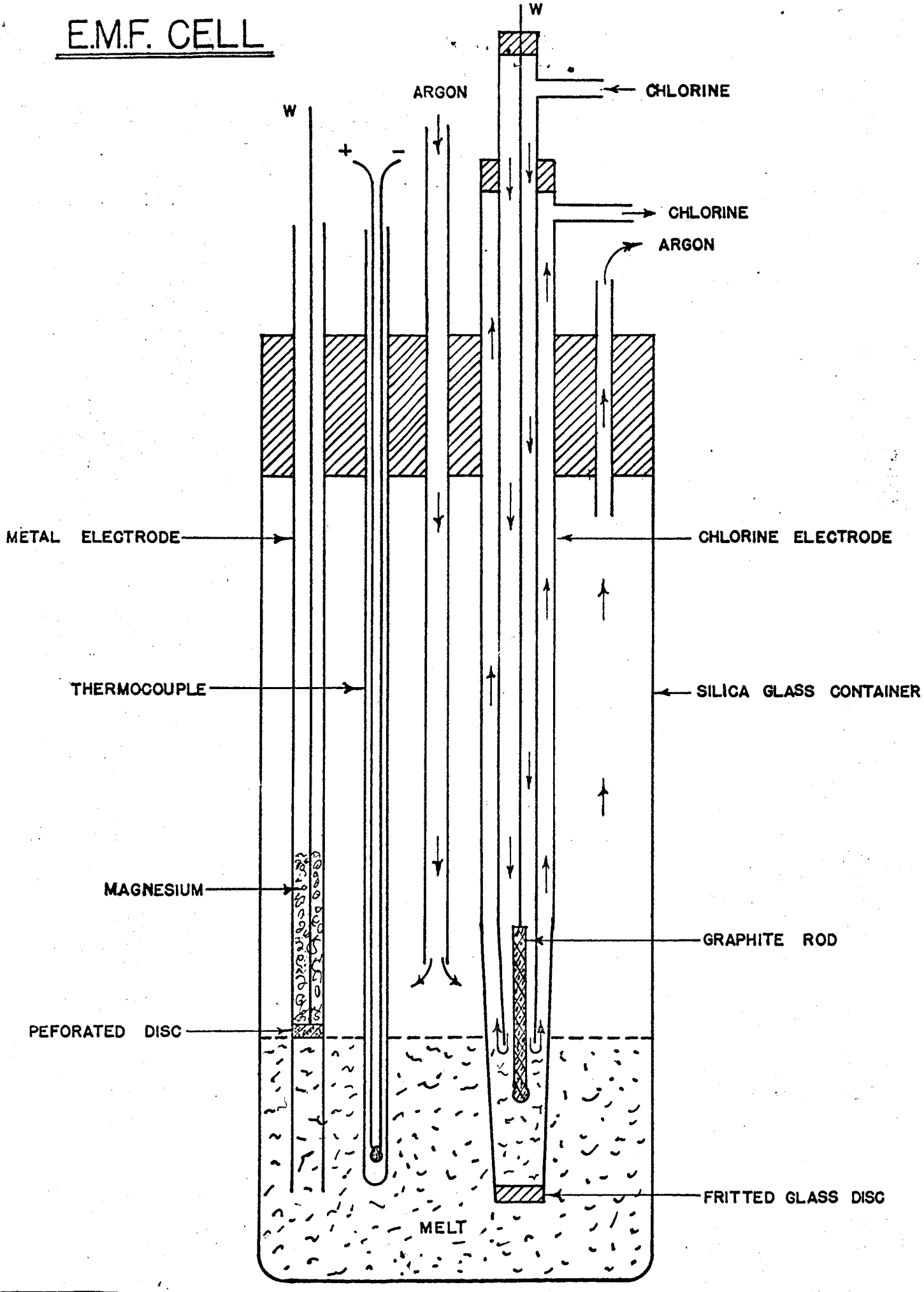


FIG. 4


(4 CYCLE LOG SCALE)
V—LOG I RELATIONSHIP OF OXIDATION OF VAD
400
640
300
540
200
440
MV
VS
SCE
100
340
240
−100
140
−200
40
.001
.0001
LOG i M AMPS
0.01
.001
0.1
.01
1.0
.1
TEMP. 37° C
PH 7.4
0.1M
PHOSPHATE
BUFFER
2 MG LAD/100 CC

E.M.F. CELL


W
ARGON
CHLORINE
W
+
−
CHLORINE
ARGON
METAL ELECTRODE
CHLORINE ELECTRODE
THERMOCOUPLE
SILICA GLASS CONTAINER
MAGNESIUM
GRAPHITE ROD
PEFORATED DISC
FRITTED GLASS DISC
MELT